

# Comment on 'Pulsed field studies of the magnetization reversal in molecular nanomagnets'

W. Wernsdorfer<sup>1</sup>, N. E. Chakov<sup>2</sup>, and G. Christou<sup>2</sup>

<sup>1</sup>*Laboratoire Louis Néel, associé à l'UJF, CNRS,  
BP 166, 38042 Grenoble Cedex 9, France*

<sup>2</sup>*Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, US*

(Dated: 30 April 2004)

## Abstract

In a recent paper, <http://xxx.lanl.gov/abs/cond-mat/0404041>, J. Vanacken et al. reported experimental studies of crystals of Mn<sub>12</sub>-ac molecular nanomagnets in pulsed magnetic fields with sweep rates up to 4000 T/s. Steps in the magnetization curve were observed. The data were explained by collective dipolar relaxation. We give here an alternative explanation that is based on thermal avalanches triggered by *defect* molecules (faster relaxing species). These species are always present in Mn<sub>12</sub>-ac molecular nanomagnets. We propose a simple method to test this interpretation. Note also that we do not question the possibility of collective effects that are based on spin-spin interactions.

PACS numbers: 75.45.+j, 75.60.Ej, 75.50.Xx, 42.50.Fx

In a recent paper, <http://xxx.lanl.gov/abs/cond-mat/0404041>, J. Vanacken et al. reported low temperature magnetization studies of  $\text{Mn}_{12}$ -ac single crystals at a field sweep rate up to 4000 T/s [1]. Their main finding was that at such high sweep rates the position of the steps in the magnetic relaxation shifts by  $\Delta H$  that increases as the sweep rate goes up. The authors scaled the relaxation curves obtained at different sweep rates onto one curve. The scaling was explained within a model of collective magnetic relaxation of the crystal.

Instead of commenting on the interpretations by J. Vanacken et al. [1], we point out here important facts about  $\text{Mn}_{12}$ -ac that may have disrupted their experiments and propose an alternative explanation that is based on thermal avalanches triggered by *defect* molecules (faster relaxing species). These species are always present in  $\text{Mn}_{12}$ -ac molecular nanomagnets. We then propose a simple method to test this interpretation. Note also that we do not question the possibility of collective effects that are based on spin-spin interactions [2]. Such effects can lead to 'off resonance' tunneling in the case of sufficient energy level mixing (activated levels, high fields, etc.).

Fig. 1 shows typical hysteresis loops [3] for a single crystal of  $\text{Mn}_{12}$ -ac. The cryostat temperature was about 60 mK. When the applied field is near an avoided level crossing, the magnetization relaxes faster, yielding steps separated by plateaus [4, 5]. The loops show two series of steps: in the low field region (0 to 2 T) and in the high field region (2.5 to 5 T). It is now well known [6] that the steps in the low field region are due to faster relaxing species whereas the others are due to the *normal* species of  $\text{Mn}_{12}$ -ac [4, 5]. The step heights decrease for faster field sweep rates. However, concerning the four fastest field sweep rates, a thermal avalanche [16] is observed at about 4 T that reverses the entire magnetization in a time scale faster than a millisecond (the time resolution of the lockin amplifier). The avalanche field decreases for faster sweep rates but the avalanche is always observed close to a resonance field.

When comparing the measurements in Fig. 1 with the pulsed field ones of J. Vanacken et al. (Fig. 2 in [1]), we note that their field sweep rates are more than 1000 times larger than our rates. Furthermore, our crystal size is much smaller than in [1]. Both points should enhance the thermal avalanche effect in the pulsed field experiment. We also note in the experiment by Vanacken et al. that the entire magnetization reverses in a time scale of about 0.2 ms and in the low field region (below 2 T) (see Fig. 2 in [1]). We propose therefore that this fast magnetization reversal could have been triggered by the heat emission of the

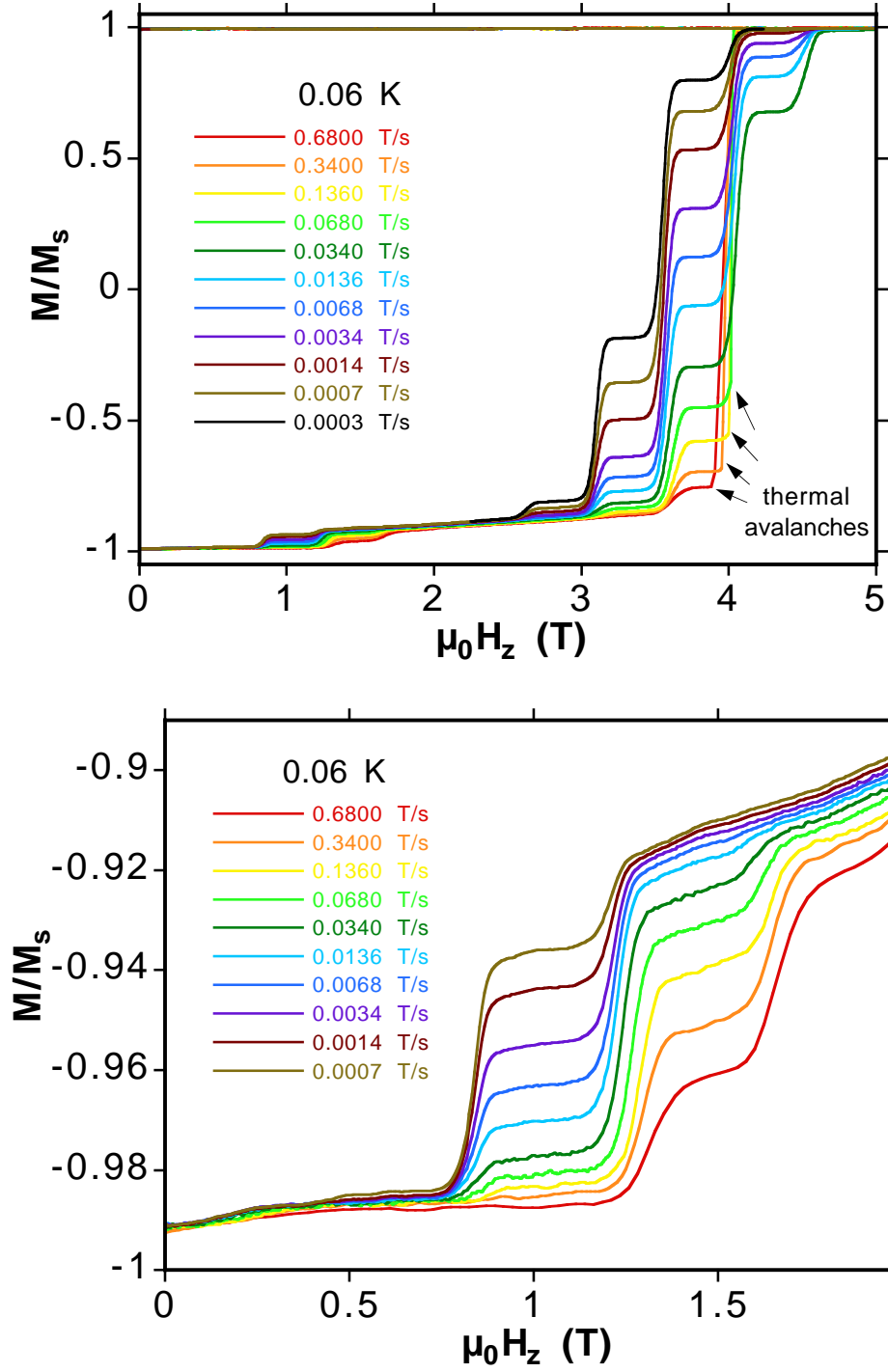


FIG. 1: (color) (a) Hysteresis loop measurements for a single crystal of  $Mn_{12}$ -ac at several field sweep rates. The field was applied at an angle of about  $6^\circ$  in respect to the easy axis of magnetization. (b) Enlargement for the low field region showing the relaxation of the fast species.

fast relaxing species reversing below 2 T [21]. The field sweep rate dependence of the step position could reflect the time needed to trigger the thermal avalanche.

This interpretation can be checked with the following method. First, a high negative field should be applied to saturate the magnetization. Then, the field should be swept slowly up to 2 T reversing only the fast relaxing species. Finally, the field should be ramped to zero field and a positive field pulse applied. The magnetization reversal should then occur above 3 T because the fast relaxing species cannot trigger any more a thermal avalanche. Note that all relevant tunnel splittings of the *normal* species are too small to induce a significant reversal below 3 T and below 0.6 K. We do not expect therefore an thermal avalanche below about 3 T.

---

- [1] J. Vanacken et al., <http://xxx.lanl.gov/abs/cond-mat/0404041>.
- [2] W. Wernsdorfer, S. Bhaduri, R. Tiron, D. N. Hendrickson, and G. Christou, Phys. Rev. Lett. **89**, 197201 (2002).
- [3] All measurements were performed using a 2D electron gas micro-Hall probe. The high sensitivity allows the study of single crystals of SMMs of the order of 10 to 500  $\mu\text{m}$ . The sample of the present study was  $20 \times 6 \times 5 \mu\text{m}^3$ . The field can be applied in any direction by separately driving three orthogonal coils.
- [4] A.D. Kent, Y. Zhong, L. Bokacheva, D. Ruiz, D.N. Hendrickson, and M.P. Sarachik, EuroPhys. Lett. **49**, 521 (2000).
- [5] I. Chiorescu, R. Giraud, A.G.M. Jansen, A. Caneschi, and B. Barbara, Phys. Rev. Lett. **85**, 4807 (2000).
- [6] Several authors have pointed out that in the  $\text{Mn}_{12}$  carboxylate family different isomeric forms give rise to different relaxation rates. This was first observed in  $\text{Mn}_{12}\text{-ac}$  [7, 8, 9, 10] and has been studied in detail [11, 12, 13, 14]. We found that a minor species of  $\text{Mn}_{12}\text{-ac}$  [15], randomly distributed in the crystal, exhibits a faster relaxation rate which becomes temperature independent below 0.3 K.
- [7] D. Ruiz, Z. Sun, B. Albela, K. Folting, J. Ribas, G. Christou, and D. N. Hendrickson, Angew. Chem. Int. Ed. Engl. **37**, 300 (1998).
- [8] S. M. J. Aubin, N. R. Dilley, M. B. Wemple, G. Christou, and D. N. Hendrickson, J. Am.

- Chem. Soc. **120**, 839 (1998).
- [9] Z. Sun, D. Ruiz, E. Rumberger, C. D. Incarvito, K. Folting, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Inorg. Chem.* **37**, 4758 (1998).
  - [10] Z. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, B. Maple, G. Christou, and D. N. Hendrickson, *Chem. Commun.* 1973 (1999).
  - [11] S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Rumberger, I. A. Guzei, K. Folting, P. K. Gantzel, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Inorg. Chem.* **40**, 2127 (2001).
  - [12] S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Rumberger, I. A. Guzei, K. Folting, P. K. Gantzel, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Polyhedron* **20**, 1139 (2001).
  - [13] M. Soler, W. Wernsdorfer, Z. Sun, D. Ruiz, J. C. Huffman, D. N. Hendrickson, and G. Christou, *Polyhedron* **22**, 1783 (2003).
  - [14] M. Soler, W. Wernsdorfer, Z. Sun, J. C. Huffman, D. N. Hendrickson, and G. Christou, *Chem. Commun.* 2672 (2003).
  - [15] W. Wernsdorfer, R. Sessoli, and D. Gatteschi, *EuroPhys. Lett.* **47**, 254 (1999).
  - [16] When studying transitions to excited states by applying a longitudinal field, phonons are created that can be absorbed by other molecules and therefore induce further excited state tunneling. The first studies of this effect was reported by Paulsen and Park [17, 18]. They observed avalanches which can reverse the magnetization of the entire crystal of Mn<sub>12</sub> acetate in a few milliseconds. More recently, Fominaya et al. [19] have recorded heat emissions at the resonant fields. Del Barco et al. [20] studied Mn<sub>12</sub>-ac in pulsed fields and found also thermally induced avalanches.
  - [17] C. Paulsen and J.-G. Park, in *Quantum Tunneling of Magnetization-QTM'94*, Vol. 301 of *NATO ASI Series E: Applied Sciences*, edited by L. Gunther and B. Barbara (Kluwer Academic Publishers, London, 1995), pp. 189–205.
  - [18] C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, *J. Magn. Magn. Mat.* **140-144**, 379 (1995).
  - [19] F. Fominaya, J. Villain, P. Gaudit, J. Chaussy, and A. Caneschi, *Phys. Rev. Lett.* **79**, 1126 (1997).
  - [20] E. del Barco, J. M. Hernandez, M. Sales, J. Tejada, H. Rakoto, J. M. Broto, and E. M. Chudnovsky, *Phys. Rev. B* **60**, 11898 (1999).
  - [21] Relaxation at non-zero field leads always to a release of energy. In the case of J. Vanacken

et al., all molecules reverse in a time window of 0.2 ms, at about 1.5 T. This leads to an energy release of  $2 \times g\mu_B/k_B S \times 1.5 \text{ T} = 40 \text{ K}$  per molecule. Knowing that there are about 5% of faster relaxing species, the energy released by it is quite important and might trigger the avalanche.